Study on photocatalytic hydrogen evolution on InP suspension with inorganic sacrificial reducing agent

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Photoelectrochemical water decomposition has been extensively studied in view of energy conversion of solar light to clean, storable chemical fuel of hydrogen. So far, only a few semiconductor photocatalysts, which are represented by TiO_2, have been reported to decompose water without applying additional external voltage. In contrast to this difficulty, it has been known that hydrogen or oxygen can be generated far more easily with the assistance of sacrificial reducing or oxidizing agent. For hydrogen generation, for example, TiO_2 can evolve hydrogen from aqueous solutions which contain organic materials such as methanol, ethanol, or formic acid as reducing agents. Besides such organic materials, inorganic ions such as sulfite or sulfide have also been reported to be able to serve as sacrificial reducing agents. The process with sulfite ion is useful in that hydrogen can be produced with concomitant reduction of the polluting material of sulfur dioxide. For the efficient utilization of solar light, it is important to employ semiconductors which have well matched band gaps with the solar spectrum. TiO_2 can absorb only a very small part of the whole solar radiation. Because InP has the bandgap of 1.25 eV and its conduction band edge is located sufficiently above standard hydrogen electrode level, InP can be expected to serve as an efficient semiconductor for photocatalytic hydrogen evolution. Here we report on photocatalytic hydrogen evolution on InP suspension with the use of inorganic sacrificial reducing agent such as sulfite ion. Reaction conditions concerning the hydrogen evolution rate have been investigated.

Characterization and Applications of Photoelectrochemically Tailored TiO_2

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We have already reported that the photoelectrochemical etching (photoetching) of a TiO_2 electrode in sulfuric acid solution generates nano-structured surface (named "nano-honeycomb" structure).[1,2] Another interesting finding is its potential dependent etching site selectivity, *i.e.*, a preferential photoelectrochemical dissolution of grain bulk for a sintered pellet TiO_2 electrode under weak anodic polarization (upward band bending), which results in the formation of a "skeleton" structure consisting of only grain boundaries.[3] The latter must offer a possibility of characterize grain boundaries, which are known to play a crucial role in some ceramic devices.

In the present work, we report more detailed characterization of grain boundary of a sintered pellet TiO_2 as well as the size control of the "nano-honeycomb".

Varying the photoetching conditions such as photoetching time, photoetching potential and light intensity did not change the size of a "nano-honeycomb", suggesting that its size is a reflection of the intrinsic property of the TiO_2 used. Modifying the properties of TiO_2 would change it. Actually upon increasing the donor density of a TiO_2 electrode by reducing it in H_2 atmosphere, the size of the "nano-honeycomb" decreased. For a TiO_2 electrode with a donor density of the order of 10^{21} cm ^{3}, the size amounts to 30 nm. The formation of such a fine structure will find useful applications to various devices such as (photo)catalysts, sensors and dye-sensitized solar cells.

HRTEM photographs of grain boundary specimens (thin platelet samples) collected from the "skeleton" have shown that grain boundary formed between two grains consists of two layers (bilayer structure), where each layer reflects each grain's crystallographic orientation. The thickness of these thin platelet samples left undissolved is about 10 nm. Detailed crystallographic properties of these samples have been analyzed, which will be discussed in the presentation.

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Photo- and Chemo-Stimulated Surface Processes and Surface Luminescence on Zirconia Particles

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Abstract

This study reports on adsorboinduced luminescence caused by dissociative adsorption of H_2 on photoactivated surfaces of zirconia, ZrO_2. Pre-photoexcitation of dispersed zirconia by UV-light stimulates formation of surface active centers for adsorption of O_2 and H_2; the lifetimes of these centers are greater than ca. 2000 s. Previous results suggest that these center are V-type hole centers for hydrogen adsorption and F-type and Zr^{3+} electron centers for oxygen adsorption. Adsorbed oxygen can be removed partially from the particle surface during photostimulated desorption caused by oxygen (as $O_2^{-\bullet}$) charge neutralization by generated photoholes (eqn 1). The apparent desorption

$$O_2^{-\bullet} + h^+ \rightarrow O_2\,(g) \qquad (1)$$

cross-section is ca. 2×10^{-18} cm^2. A consequence of pre-excitation of ZrO_2 particles is the emission of a broad green phosphorescence (around 485 nm) caused by trapping of free electrons by anion vacancies (eqn 2). The decay time of this luminescence is ~ 15 s which corresponds to the mono-molecular thermoionization of shallow traps with energy $E_i \approx 0.6$ eV.

$$e + V_a \rightarrow F^* \rightarrow F + h\nu_{em.} \qquad (2)$$

Dissociative adsorption of H_2 on hole surface centers is accompanied by a luminescence light pulse which decays by double exponential kinetics ($\tau_1 = 0.9$ s, $\tau_2 = 15$ s). The spectrum and the decay time of this photoinduced adsorboluminescence (PhIAL) are identical to the phosphorescence spectrum and decay time of the emission from ZrO_2 following direct illumination in the *intrinsic* absorption region (5.0 eV).Consequently, we infer that the chemical steps (eqns 3–6) cause energy release that is transferred efficiently to the solid by energy (eqns 4,5) or charge transfer (eqn 6).

$$O^{-\bullet}_s + H_2 \rightarrow OH^-_s + H^\bullet \qquad (3)$$
$$H^\bullet + H^\bullet \rightarrow H_2^* + ZrO_2 \rightarrow ZrO_2^* \rightarrow e + h \qquad (4)$$
$$H^\bullet + O^{-\bullet}_s \rightarrow OH^{-*}_s + ZrO_2 \rightarrow ZrO_2^* \rightarrow e + h \qquad (5)$$
$$H^\bullet + O^{2-}_s \rightarrow OH^-_s + e \qquad (6)$$

Chemo-stimulated processes produce additional electron surface centers for O_2 adsorption. Moreover, another result of H_2 addition is removal of some forms of pre-adsorbed O_2 from the surface which coincide with those forms removed during photodesorption of O_2.Therefore, we infer that in relation to certain events (e.g. luminescence, formation of surface centers, adsorbed O_2 reactivity) photo- and chemo-stimulated surface processes behave similarly. They can be applied to increase both the photoactivity and photosensitivity of metal-oxide solids using the highly energetic chemo-stimulated surface processes.

INVESTIGATIONS OF CERAMIC Fe_2O_3<Ta> PHOTOELECTRODES FOR PHOTOELECTROCHEMICAL CONVERSION OF SOLAR ENERGY

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A possibility of photoelectrochemical conversion of solar energy in the process of the photoelectrolysis of water in energy of high caloric fuel (hydrogen) was stimulated investigations of semiconductor photoelectrodes as photocatalysts of the reaction mentioned above and investigations of properties and structure of the semiconductor - electrolyte interface too.

In present work the ceramic semiconductor Fe_2O_3 photoelectrodes doped with different concentration of Ta (from 0,1 up to 2 At. %) are manufactured and investigated. The prospects for the use of these photoelectrodes for the water photodecomposition in hydrogen and oxygen is connected with their high photoresponse in the visible range of the solar spectrum, stability to photocorrosion, cheapness and rather simple technology of manufacturing of polycrystalline samples.

The results of investigation of electrophysical and photoelectrochemical characteristics of the Fe_2O_3<Ta> photoelectrodes depending on the contents of impurity are presented. The temperature dependence of the conductivity as well as spectral, current-voltage and capacitance-voltage characteristics are investigated. The charge carriers concentration, donor centers activation energy, flat band potential of electrodes are determined.

The investigations of properties of the Fe_2O_3<Ta> - electrolyte interface are carried out by the electrochemical impedance spectroscopy method. Analysis of the frequency dependencies of the real and imaginary parts of complex impedance allowed to determine the equivalent circuit of the photoelectrochemical cell and calculate the parameters of components of the circuit. Ways of an improving of the photoelectrochemical properties of photoelectrodes made of Fe_2O_3 doped with Ta, are determined.

Electrochemical Deposition of Organic Semiconductors on Nanoporous TiO_2 Electrodes for Solar Cells

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The use of organic semiconductors (OSC) in photovoltaic cells has shown low efficiency of solar energy conversion[1,2]. Light absorption in these cells results in exciton creation that reacts with an electron (or hole) selective material that dissociates (quenches) the exciton and enables usable charge separation[1]. To complete the circuit, the charges have to be collected by migration across the OSC and quencher layers. This process is dominated by the high electrical resistivity of the OSC[3]. Efficient charge separation depends therefore, on the exciton diffusion length, the quality of the selective quencher and the quality of the OSC-quencher interface[4,5]. Efficient light conversion depends also on the OSC resistivity and the charge migration length[1].

One of the promising OSC-quencher combinations for solar cells is the PPEI (Perylene Bis(phenethylimide))–ZnPC (zinc phthalocyanine) system[1,6]. In this system the exciton diffusion length in the PPEI is larger than 2.5 micron and the qualities of the hole selective quencher and the OSC-quencher interface are good[1]. However, these cells suffer from high electrical resistivity of the OSC, which limits the thickness of the PPEI layer[1]. As a result of the thickness limitation, the optical density and thus the conversion efficiency of the cells reported so far are low.

One of the ways to increase the optical density without thickening of the PPEI layer is to increase the surface area of the cell using porous substrates. However, this approach necessitates the ability to deposit the OSC into porous material, a requirement that cannot be achieved using the standard deposition method i.e. evaporation in high vacuum[3]. We have developed a new method that enables fabrication of OSC layers in porous substrates. The method is based on electrochemical deposition of PPEI ions that are electrochemically produced during the deposition process. Using this method, we deposited PPEI inside nanoporous TiO_2 electrodes[7]. It was found that both the ionization and the deposition parameters determine the physical properties of the resulting film.

The new electrode was tested in a solar cell configuration using liquid electrolyte as a quencher. The IPCE measurements show photovoltaic activity throughout the wide absorption spectrum of the PPEI layer. This is the first step towards fabrication of efficient solid state solar cells that is based of OSC.

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A Photoelectrochemical Cell Using Self-Assembled Monolayers

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Solar energy conversion is basically important for the creation of clean energy systems. Organic molecules are relatively cheap and very useful for collecting UV-visible light, as has been verified by a dye-sensitized solar cell. [1)] Construction of highly-ordered assemblies of photoactive molecules is basically important for successful applications of organic molecules to the cell device. We report here a photoelectrochemical cell using self-assembled molecular layers of ruthenium tris (2,2'-bipyridine) - viologen pair.

The ruthenium tris (2,2'-bipyridine) (Ru), viologen (V), and their linked disulfides were prepared in our laboratory. As a typical example, the self-assembled monolayer of the Ru-V linked thiol was prepared on an ITO electrode, by immersing the ITO electrode into the sample solution for 4 days. A photoelectrochemical cell consisting of the modified electrode and the counter ITO electrode, with 12.5 μm spacing each other by using a polyimide film, containing the iodine / triiodine redox electrolyte in ethylene glycol, was constructed. The light from the Xenon lamp irradiated the cell, and the resultant photocurrent was detected by a potentiostat. Anodic photocurrents were clearly obserbed. The photocurrent action spectrum corresponded well the absorption spectrum of the complex in solution, indicating the Ru-sensitized photoredox cycles. The distance between the Ru and the V moieties also affected photocurrents: larger for a larger Ru-V distance. However, the photocurrent was not so large as expected: one of the reasons is relatively low fractional coverage ($\sim 10^{-11}$ mol/cm^2). Optimization of the electrolyte as well as the cell thickness are in progress.

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Water splitting using a novel series of photocatalysts, NiO_x-$InNbO_4$ and NiO_x-$InTaO_4$ under visible light irradiation

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The photocatalytic water splitting using oxide semiconductor materials under visible light irradiation attracts an increasing interest because the attempt is aimed not only at producing hydrogen of clean-energy from water utilizing solar energy, but also at finding methods of making use of the photosynthetic process as green plants for direct production. Here, we firstly report the observation of pure water splitting by a novel series of prepared 0.5wt%NiO_x-$InTaO_4$ and 0.5wt%NiO_x-$InNbO_4$ photocatalysts under visible light irradiation.

The polycrystalline samples of $InNbO_4$ and $InTaO_4$ were prepared by solid state reaction method. The band gaps of $InTaO_4$ and $InNbO_4$ were estimated to be about 2.6 and 2.7eV by UV-vis diffuse reflectance spectrum measurement. The typical experimental conditions of photocatalytic reaction are as follows: 0.5wt% nickel oxide was loaded on $InNbO_4$ and $InTaO_4$ powders from aqueous $Ni(NO_3)_2$ solution by an impregenation method. Catalyst was calcined at 350^o in the air then reduced at 250^o under the H_2 stream. The 0.5g of powder catalyst ($InNbO_4$ or $InTaO_4$ loaded 0.5wt% nickel oxide) was suspended in a 120 ml of pure water in a Pyrex glass cell (200ml). A 300W Xe arc lamp was focused through a shutter window and a 420 nm cut filter onto the window face of the cell.

The formation rates of H_2 evolution were about 3.5 and 4.0 $\mu mol.g^{-1}.h^{-1}$ for 0.5wt%NiO_x-$InNbO_4$ and 0.5wt%NiO_x-$InTaO_4$, respectively, under visible light irradiation more than 420 nm. The H_2 evolution lasted even after 200 hours. The H_2 evolution stopped when the irradiation was terminated, showing the obvious visible light response. Oxygen evolution was not observed. We speculated the photoadsorption of produced oxygen over the photocatalysts. It was suggested that produced oxygen photoadsobed on the surface of these photocatalysts from the measurement of magnetic susceptibility (χ/T) of used photocatalysts. The crystal structure was investigated using an X-ray powder diffraction. All samples are with a similar crystal structure: wolframite type, monoclinic with space group P2/c. The lattice parameters of $InNbO_4$ before and after reactions are the same, $a = 4.843$, $b = 5.773$, $c = 5.147$Å *and* $b = 91.14^o$. The lattice parameters of $InTaO_4$ before and after reactions are also same, but they are slightly different to those of $InNbO_4$, with $a = 4.833$, $b = 5.778$, $c = 5.157$Å *and* $b = 91.23^o$. The chemical composition of these samples was examined by the SEM-EDS method. The average rates of In:Nb and In:Ta were 1.0:1.05 and 1.0:1.04. From these experimental results we confirmed that these photocatalysts before and after reactions have not changed in both the crystal structure and the chemical composition. It is firstly demonstrated that water could be decomposed to H_2 and O_2 using NiOx-$InNbO_4$ and NiOx-$InTaO_4$ photocatalysts under visible light irradiation.

Novel Photovoltaic Cell Using an "n-Si / Metal Island / CuI" Junction

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The main target in recent solar-cell studies is to fabricate high-efficiency and low-cost solar cells. The conversion efficiencies exceeding 20% have been reported using high-quality single-crystal Si with elaboration of the cell structure by photolithographic techniques, but such cells may not meet the requirement of low cost. Another most promising approach is to use low-cost polycrystalline Si thin films. The problem is how a high-quality junction can be formed for such row materials having geometrically rough surfaces and many grain boundaries. We have developed solar cells of a new type, equipped with an n-Si electrode with nano-sized Pt dots and an HBr/Br_2 redox electrolyte. The cells generated open-circuit photovoltages (V_{oc}'s) higher than the conventional p-n junction Si solid solar cells with a similar simple structure. The principle can be extended to solid-state solar cells and applied to polycrystalline Si thin films.

In this study, we applied a cuprous iodide (CuI) layer to fabricate a solid-state photovoltaic juction on n-Si with metal dots. The CuI layer was formed by vacuum deposition. An ITO glass was attached on the CuI to obtain an electrical contact for the solar cell. The solid curve of the figure shows a photocurrent-voltage characteristic of the n-Si/CuI junction without metal dots under illumination of AM1.5, 100 $mWcm^{-2}$. A high V_{oc} of 0.617 V is obtained, which is close to a theoretical value expected for a minority-carrier controlled solar cells, implying that an ideal junction is formed at the n-Si and CuI interface. The broken and dot-dashed curves are for n-Si with Pt and Au dots, respectively. At present, the metal deposition led to decreases in V_{oc} most probably because of aggregation of the metal particles on n-Si, resulting in large clusters as confirmed with an SEM. The metal deposition is expected to play an important role in obtaining the long-term stability, similarly to the case of photoelectrochemical solar cells.

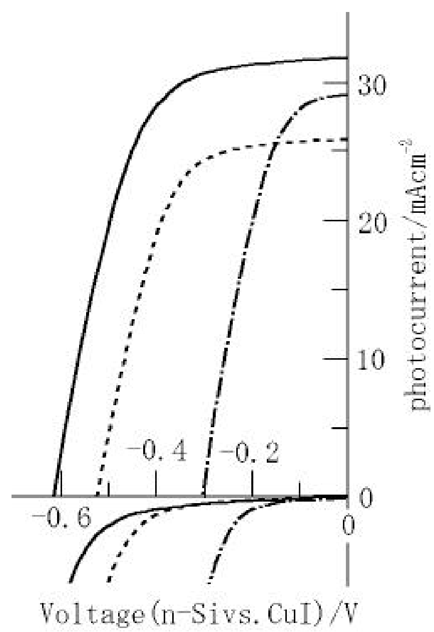

Figure. Photocurrent-voltage chracteristics of n-Si / metal island / CuI photovoltaicc cell under illumination using AM 1.5; without metal deposion (solid line), Pt deposited (doted line), Au deposited (doted-broken line).

Effect of halide ions upon photooxidation reactions at a WO_3 photoanode

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In spite of their more positive oxidation potential, chloride ions are known to undergo preferential photooxidation (with respect to water) at a tungsten trioxide photoanode[1], at least from relatively concentrated solutions. However, our recent observation that even addition of small amounts of chloride and, especially, bromide ions to various acid solutions affected markedly the onset potential of the photocurrent, the rising portion of the photocurrent-voltage curve and the amount of the saturation photocurrent at nanosized WO_3 photoelectrodes, prompted us to re-examine their effect in more detail. Experiments performed using 2-3 μm thick WO_3 films showed that although the faradic efficiency for the formation of Cl_2 reached ca. 60 % in 4 M NaCl solution (acidified to obtain pH 1-2) it decreased to 25-30 % in 0.1 M NaCl. This is not enough to account for a large (more than twofold) increase of the saturation photocurrent following the addition of 0.01-0.1 mol/L of NaCl to 1 M solution of $HClO_4$. Similar effect upon the photocurrent is actually observed after the addition to 1 M $HClO_4$ of only 0.001 mol/L of NaBr. These results strongly suggest that Cl^-, Br^- (and also I^-) ions act, in fact, as promoters of the photooxidation of water at WO_3. Prolonged photoelectrolysis of a 1 M $HClO_4$ solution at a WO_3 photoanode, exposed to a simulated solar irradiation, results in a progressive decrease of the photocurrent. However, the initial activity is completely restored either by a short cathodic reduction sequence or by a prolonged illumination of the WO_3 film with UV light under open-circuit conditions. The above mentioned decrease of the photocurrent is no more observed when the $HClO_4$ solution contains even a small (0.01 M) amount of Cl^- (or Br^-) ions. This activating effect of halides may be associated with their well known redox reactivity towards peroxo complexes of tungsten (VI) [2].

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Electroless Deposition of Fine Pt Particles on n-Si from HF Solutions for Efficient Photoelectrochemical Solar Cells

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Photoelectrochemical solar cells using an n-Si electrode modified with ultrafine Pt particles generate high open-circuit photovoltages (V_{OC}'s) of 0.62-0.68 V and give high conversion efficiencies of 14-15 %.[1,2] Electroless deposition has the advantages of low cost process and uniform deposition. Various metals can be deposited on Si from simple solutions of HF and metal salts.[3,4] In this study, the electroless deposition has been applied to the modification of n-Si electrodes with ultrafine Pt particles for developing the high-efficiency and low-cost solar cells.

Single crystal n-Si wafers (CZ, (100), ca. 1 Ωcm) were washed with acetone and etched with CP-4A and HF. The n-Si wafers were immersed in aqueous HF solutions including H_2PtCl_6. Solar cell characteristics were measured in 8.6 M HBr/0.05 M Br_2 aq. under illumination with a tungsten-halogen lamp. The illumination intensity was adjusted such that it gave the same photocurrent as simulated solar illumination (AM 1.5G, 100 $mWcm^{-2}$) for single crystal Si solar cells.

Fig. 1 shows a SEM for an n-Si electrode modified with electrolessly deposited Pt particles by immersing in the solution of 1 mM H_2PtCl_6 and 15 mM HF for 120 s at 30 ℃. The size and distribution density of Pt particles are 0.05 to 0.3 μm and 3×10^8 particles cm^{-2}, respectively. The density of Pt particles changed with the deposition conditions such as the concentrations of H_2PtCl_6 and HF, the immersion time of n-Si, and the temperature of deposition solution. The solar cell characteristics of n-Si electrodes modified with fine Pt particles changed with the size and density of the particles. V_{OC} of 0.55-0.58 V and the maximum power output of 9.1-10.5 $mWcm^{-2}$ were obtained for n-Si electrodes modified with Pt particles under the above condition. The heat treatment (100-150 ℃) of Pt-deposited n-Si electrodes improved the fill factor of the solar cells.

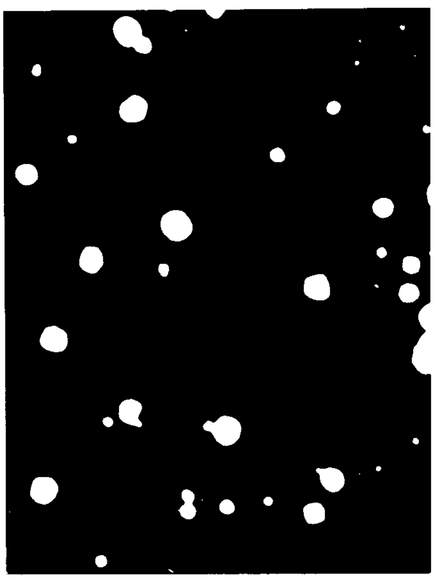

Fig. 1. SEM for a Pt-deposited n-Si.

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REACTION PATHWAYS INVOLVING METAL IONS AND SELENIUM(IV) SPECIES IN UV-IRRADIATED TITANIA AQUEOUS SUSPENSIONS

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That a variety of organic and inorganic substrates can be photooxidized and photoreduced in UV-irradiated TiO_2 aqueous suspensions is now well-established. Much less is known about the photocatalytic reaction pathways undergone by metal ions with rather negative standard reduction potentials such as Zn(II), Cd(II), and even Pb(II). Photocatalytic reactions involving chalcogenic species [e.g., Se(IV)] also have received little attention. This paper presents scenarios affording facile reduction of the above substrates to the elemental form. Further, the underpotential reduction of these metal ions in the presence of an initial selenium layer on the TiO_2 surface facilitates a new preparation strategy for coupled MSe/TiO_2 semiconductor particles or films. Data on interesting interfacial changes (in the dark and under UV irradiation) will be presented for formate and ammonium ion addition to TiO_2 aqueous suspensions containing either Zn(II) or Cd(II). Careful consideration of these results leads to new insights into reaction pathways in UV-irradiated titania suspensions in general.

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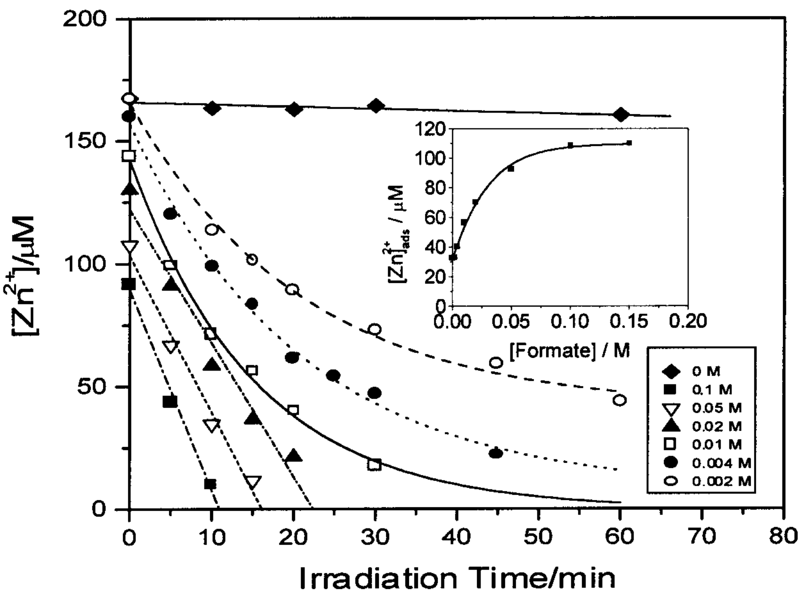

Fig. 1. Influence of formate addition (at the levels shown) on the conversion of Zn(II) in N_2-sparged TiO_2 suspensions under UV-irradiation. The insert contains adsorption data in the dark.

Sonophotocatalytic decomposition of water using $BiVO_4$ photocatalyst

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1.Introduction

Photocatalytic decomposition of water is very attractive from the view point of solar energy conversion. In recent years, ultrasonic irradiation effects on heterogeneous photocatalytic reaction systems have been reported and it has found that pure water is decompose to H_2 and O_2 by the simultaneous irradiation of light and ultrasound in the presence of TiO_2 [1]. Titanium oxide is often used as a photocatalyst because of its stability in solution, reasonable cost, and low poisonous characteristics. Because of large bandgap, however, it is difficult to perform the reaction using visible light. In this paper, the possibility of the sonophotocatalytic decomposition of water using visible light and ultrasound was examined.

2.Experimental

As the powdered photocatalysts, $BiVO_4$, CdS and Fe_2O_3 were used. $BiVO_4$ was synthesized by aqueous processes[2]. Simultaneous irradiation was performed from one side with a 500-W Xe lamp with an attached Y-43 filter(>430 nm) and from the bottom surface with a 200-W ultrasonic generator (200 kHz.) under argon atmosphere at 25° C. The amounts of gaseous reaction products were analyzed by gas chromatography.

3.Results and discussion

In order to decompose pure water, a photocatalyst suspended in pure water was performed with the simultaneous irradiation of visible light(>430 nm) and ultrasound. In the case of $BiVO_4$, H_2 and O_2 were evolved continuously as shown in Fig. 1. The product ratio was nearly 2.0 after an induction period.

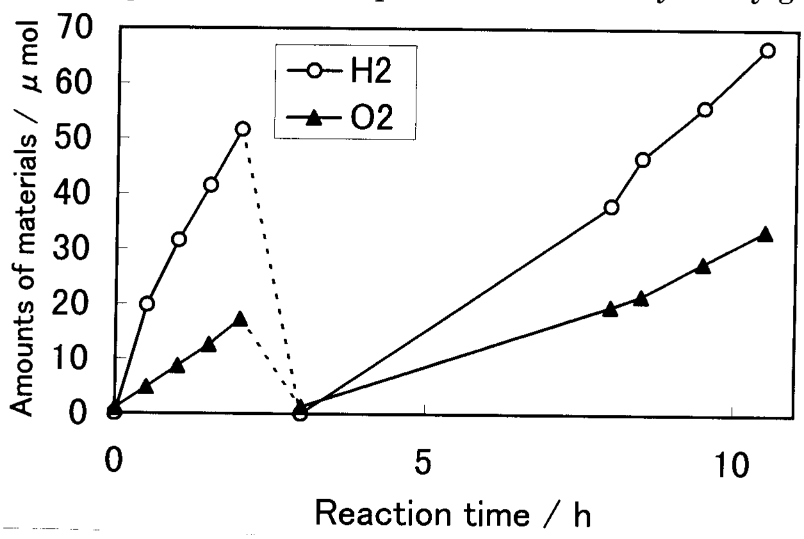

Fig.1 Sonophotocatalytic reaction products from water using $BiVO_4$ photocatalyst

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Drastic Photocurrent Enhancement by Proton Intercalation in Anodized TiO_2

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Photocurrent of rutile TiO_2 made by anodization of Ti metal was found to be greatly enhanced by proton intercalation and became comparable to or even larger than that of single crystalline rutile. Such effect could not be observed in anatase TiO_2. The surface state modification with proton intercalation was confirmed by EL spectra, the peak wavelength of which locates at 850 nm. When the protons thus intercalated is forced to be de-intercalated by applying a large anodic bias, the intensity of this EL band (Γx) decreased in accordance with the decrease in the photocurrent. In the meanwhile, the effects of proton intercalation could not be observed in anatase form: Namely not only the Γx band but also the photocurrent enhancement could not be observed. Since the desired crystalline form, i.e., rutile- or anatase-rich film, could be rather easily formed by changing the concentration of $Ca(CH_3COO)_2$ used in the anodization, comparative characterization between anatase and rutile structure was possible. Although the photocurrent in the intercalated-rutile film was large, its photocatalytic activity was rather low compared to the nano-size thin film made by cathodic electrodeposition, the procedure of which was proposed by us. Intercalated-rutile thin films were activated by depositing nano-particles. Both methods, i.e., anodization and electrodeposition can be done in solutions, enabling us to fabricate a large scale electrode system. Full characterization of the resultant thin films is to be made by XRD, XPS, SEM, CV, and EL.

Cathodic photo-protection of steels from corrosion by using TiO_2 thin films

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Introduction

Photocatalytic reactions of TiO_2 particles and films were extensively studied for the purification of air and water in the past decades.[1,2] Most harmful and toxic organic compounds can be oxidized to carbon dioxide with the strong oxidizing power of the photogenerated holes of TiO_2. On the other hand, if TiO_2 is in contact with a metal, irradiated TiO_2 injects electrons to the metal through the conduction band, as a result, the potential of the metal can be changed to the flatband potential of TiO_2. If the potential is more negative than the oxidation potential of the metal, the metal can be protected against corrosion. We are undertaking the cathodic photo-protection of steels by developing methods for coating TiO_2 conveniently and directly on metal substrates. In the present work, we have examined the photoelectrochemical behavior of steels coated with TiO_2 by spray-pyrolysis technique under comparatively mild conditions (sintered at around 300 °C). We evaluated the amounts of dissolved iron by spectrophotometric means to confirm the cathodic photo-protection ability against the corrosion of TiO_2-coated steels.

Experimental

Type 304 stainless steel plates of 1 mm thick were used as specimens. On the bare 304 stainless steel substrate, the TiO_2 film was prepared by a spray-pyrolysis technique from a 0.05 M ethanol solution of titanyl acetylacetonate (Tokyo Kasei) at 300 °C. The following all measurements were carried out in an aqueous solution containing 3% NaCl.

Results and Discussion

Uniform, transparent TiO_2 films were obtained under the described coating conditions. The photopotential of the TiO_2-coated sample was -0.35 V vs. Ag/AgCl, which was found to be much less positive than the corrosion potential for the bare 304 stainless steel (+0.2 V vs. Ag/AgCl). This suggests that TiO_2 can protect the 304 stainless steel from corrosion. The photopotential of this TiO_2–coated stainless steel was very stable and did not change at least for 15 hours. The photoanodic reaction proceeding at TiO_2 should be the oxidation of H_2O by the photogenerated holes in the valence band.

The sample with full coverage of TiO_2 did not corrode either under UV illumination or dark in the 3% NaCl solution at 90 °C for 12h. This behavior verifies the physical and chemical stability of the TiO_2 thin film. On the other hand, for the sample with 50% coverage of TiO_2, no corrosion was observed under UV illumination, although corrosion was appreciably observed in the dark. This means that cathodic photo-protection for 304 stainless steels was achieved as a result of the photopotential of TiO_2, and considerable defects in the film did not hinder the protection performance.

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Rate Constants of Electron Transfer Reactions at n-ZnO/Liquid Contacts

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ABSTRACT

Differential capacitance vs potential and current density vs potential measurements have been used to investigate the interfacial energetic and kinetic behavior of n-ZnO in contact with a series of one-electron, outer-sphere redox couples. A number of n-ZnO/$A^{3+/2+}$ contacts displayed almost ideal energetic and kinetic features. The rates of electron transfer were found to be first order in both the surface-electron and the dissolved redox acceptor concentration in the solution. Differential capacitance measurements indicated that the band edges remain fixed for a given ZnO electrode as the electrochemical potential of the solution was varied. The rate constants obtained in this work also compare favorably with the values predicted theoretically.

In Situ Optical Second Harmonic Generation Study at Palladium and Palladium-deposited Gold Electrodes

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As has been reported[1-2], intensity of the second harmonic (SH) light generated at platinum electrode/electrolyte interface is extremely enhanced by the chemisorption of upd-H. Recently, we observed similar potential dependent SHG enhancement at palladium electrode during hydrogen adsorption and absorption. Such an enhancement of the SH intensity by chemisorbed hydrogen has been normally understood as the resonant enhancement of SHG coupled with the interband transition from the adsorbed hydrogen states to the Fermi states of metal. For hydrogen adsorbed Pt surface, wavelength dependent studies of fundamental and SH light was not straightforward because the SH enhancement was observed at any wavelength investigated. On the other hand, the SH enhancement at hydrogen chemisorbed Pd surface was more dependent on the fundamental or SH wavelength. These facts indicated that the electronic states changed by the chemisorbed hydrogen have narrow energy distribution and the SHG measurement at Pd surface may be more sensitive to the change in the surface electronic structure.

In this study, we compared potential dependent profile of SH intensity at electrochemically Pd-depositted Au electrode and that at bulk Pd electrode. Although the current caused by the chemisorption of hydrogen was observed at Pd thin layers on Au electrode, the SH intensity was not enhanced in the wavelength region investigated. Details will be discussed in the poster session.

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Nanostructured WO_3 Thin Film Electrodes for Water Oxidation

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Abstract

Nanostructured WO_3 thin films were prepared. The electrochemical and photoelectrochemical behavior of the films were studied in aqueous solution of pH4.68 in a broad potential range and at different temperatures around room temperature. In the potential range of 0~1500 mV (*vs.* saturated Ag/AgCl reference electrode) the dark current was negligible; while at potentials above 1500 mV the oxidation of water took place, which is to some extent assigned to the leakage at back-contact. Photocurrent onset was at *ca.* 100 mV, and the saturation photocurrent was at potentials above 800 mV. In the range of 300~1000 mV, photocurrent increased linearly with the increasing light intensity, indicating that charge carrier generation is the limiting factor for the photocurrent.

The incident photon to current efficiency (*IPCE*) and the quantum yield (Φ) were high, regardless of the incidence of the light (front side EE, or back side SE illumination), indicating an efficient charge transport. Both $IPCE_{EE}$ and $IPCE_{SE}$ increased with film thickness. The long wavelength edge of the action spectra was red-shifted and moved toward the absorption band edge. Both Φ_{EE} and Φ_{SE} reached a plateau region at shorter wavelength. In the plateau, Φ_{SE} was close to 1, independent of the film thickness; while Φ_{EE} was approximately 20% lower and decreasing with increasing film thickness. By adopting a simple diffusion model for the electron transport, the diffusion length of electrons (L) was estimated.

Higher activation energies, E_A, were obtained at lower potentials, e.g., 0.60 eV at 200 mV and 0.32 eV at 300 mV. The E_A was below 0.21 eV in the range 400~700 mV, and decreased further to 0.06 eV at 1000 mV. The variation of E_A with potential was explained by the existence of a distribution of electron trapping states below the conduction band.

Keywords: photoelectrolysis, nanostructured, WO_3, electron transport

Spectroelectrochemical Study of 7,7'-Diapo-7,7'-diphenylcarotene

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As a synthetic carotenoid, 7,7'-diapo-7,7'-diphenylcarotene (**I**) and its reaction products including the cation radical and polymeric products were studied by using simultaneous optical and electrochemical techniques. Electrochemistry of **I** suggests that the polymeric products, which are generated by electrochemical oxidation of neutral **I** in dichloromethane, can be adsorbed on various electrodes. It is interesting to note that there is no such unique adsorption behavior observed for other common natural carotenoids such as β-carotene and canthaxanthin. UV-visible absorption spectra and the decay rates of cation radical and polymeric products were measured at different potentials applied during bulk electrolysis. Electrochemical reactivity of **I** on Au electrodes modified with three kinds of self-assembled monolayers (long-chain alkanethiols, ω-substituted alkanethiols and 4-mercaptopyridine) compared to bare Au electrodes is reported. The influence of the ω-functional group and thickness (chain length in *n*-alkanethiols) of the monolayer on the electrochemical reaction of **I** was explored. By comparison to bare gold electrodes, the thiol-monolayers cause a barrier effect for the reaction of **I** and the adsorption of polymeric products on the Au electrode surface. With increasing chain length of alkanethiol molecules, a stronger barrier effect to the adsorption of polymeric products is observed. This work is supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy under Grant No. DE-FG02-86-ER13465.

STRATEGY FOR IMPLEMENTING POROUS SILICON IN MULTICRYSTALLINE SILICON SOLAR CELL PROCESSING

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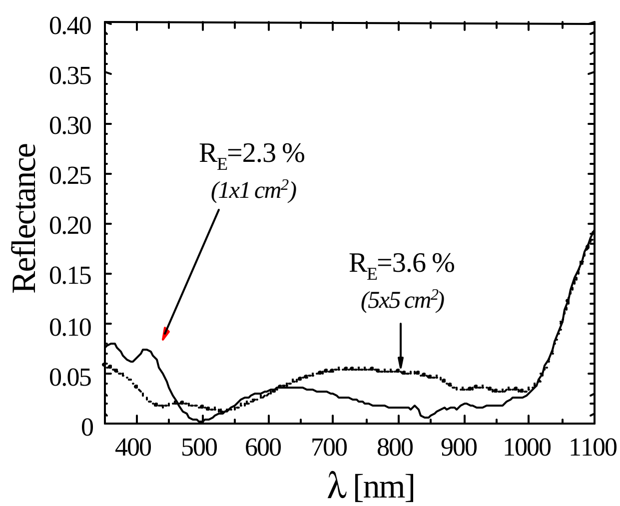
It is now well established that a porous silicon (PS) layer formed on the top of a Si solar cell can act as an efficient antireflection coating (ARC) [1]. Practically, the PS layer is formed electrochemically in HF solutions at the latter stage of the cell process, i.e. in the outer part of the emitter (n^+) on a cell with already deposited front contacts. With multicrystalline Si solar cells (Photowatt Int.) we have shown that such PS ARCs compare favorably to classical TiO_2 ARCs (cell efficiency ≥ 13 % with PS [2]). More recently, we have also demonstrated the possibility to create double-layer PS ARC by modulating the current density (i.e. the porosity) during the treatment. Such surfaces exhibit an effective reflectance of less than 4 % in the 400-1100 nm range (AM 1.5 conditions), the lowest value ever reported for PS based ARCs [3].

However, we observed that the long etching time required to form double-layer PS ARCs is deleterious to the front contacts because of the pronounced exposure to HF. Consequently, we undertook numerous experiments on PS formation over a large range of electrochemical conditions, including especially the nature of the electrolytes and their concentration. We developed new chemical solutions less harmful to the front contacts but still leading to low effective reflectance. The enclosed figure shows the reflectance of PS layers formed on multicrystalline Si (chemically polished) under different conditions, and gives their effective reflectance (R_E, 400-1100 nm range, AM 1.5 conditions). Although these experiments were carried out without modulating the current density, the shape of the reflectance spectra indicates the existence of a multiple-layer structure rather than a single-layer ARC. In this presentation, we will discussed this point in the light of simulation studies of the optical properties of multiple-layer PS ARC.



We will also present our last results on the application of these electrochemical treatments to 5x5 cm^2 multicrystalline Si solar cells. The efficiency of PS ARCs will be discussed on the basis of the photovoltaic characteristics of cells before and after treatment and in comparison to classical ARC materials. These results have been obtained in the frame of an European project which has for goal the implementation of PS at the level of an industrial process.

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Title: Stabilization of n-Si Photoanodes in Aqueous Electrolytes through Surface Alkylation.

Authors: Nathan S. Lewis*, David Michalak, Ashish Bansal

Abstract:

Stabilization of n-Si photoanodes to aqueous electrolytes has been achieved through a Grignard-like surface modification. The resistance to photooxidation and photocorrosion was corroborated through studies with n-Si in contact with $Fe(CN)_6^{3-/4-}$(aq) and with CH_3OH-$Me_2Fc^{+/o}$ containing known amounts of water. Current-voltage and capacitance-voltage measurements have shown that the alkyl terminated surfaces are very similar to the H-terminated surfaces. The alkyl layers provide a small resistance to charge transfer across the silicon/liquid interface but do not shift the band edges or induce additional surface recombination.

Photoelectrochemistry of Tris(2,2'-bipyridine) Ruthenium(II)-C_{60} dyad adsorbed on nanocrystalline SnO_2 electrodes

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The back electron transfer between the oxidized sensitizer and the semiconductor in dye sensitized photoelectrochemical (DSPE) cells remains a major problem to their development. Recently, we showed that the back electron transfer can be suppressed with the use of composite semiconductor films.[1,2] Alternatively, the use of supermolecular systems, i.e., dyads, triads, etc., composed of covalently linked donor-acceptor components, have also shown a great promise to promote long distance charge separation.[3,4], and thus slowing down the recombination process. With this objective in mind, we have fabricated a DSPE cell by depositing the dyad, tris(2,2'-bipyridine)ruthenium(II)-C_{60}, Ru(II)-C_{60}, obtained from ruthenium bipyridyl complex, Ru(II), and a fullerene C_{60}, on nanocrystalline SnO_2 electrodes, and have carried out its spectroscopic and photoelectrochemical studies.

A large quenching in fluorescence of the dyad, Ru(II)-C_{60}, relative to Ru(II), both adsorbed on SiO_2, suggests the occurrence of an intramolecular electron transfer in dyad from the Ru(II) moiety to the C_{60} moiety. However, the incident photon to current conversion efficiency (IPCE) of the dyad based PE cell, is rather inferior to that for Ru(II) based cell. This has been explained in terms of the attachment of the Ru(II) moiety of the dyad to the SnO_2 surface that leads to the creation of two opposite electron transfer pathways, and makes the electrons transferred to C_{60} from Ru(II)* go waste as far as the production of photocurrent is concerned. It is, thererore, suggested that suitable groups should be incorporated in the C_{60} moiety which can facilitate the anchoring of the dyad to SnO_2 via C_{60} moiety. This will help electrons, transferred intramolecularly from Ru(II)* to C_{60}, also generate photocurrent, and will, as a result, lead to the efficient dyad based PE solar cells.

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Salt Effects on Photoreduction of Water to Hydrogen Sensitized by *p*-Terphenyl

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p-Terphenyl (TP) sensitizes photocatalytic reduction of water to dihydrogen (H_2) under UV (λ > 290 nm) irradiation of homogeneous aqueous acetonitrile solution in the presence of triethylamine (TEA) as a sacrificial electron donor and Ru^{3+} as a precursor of co-catalyst, Ru metal colloid. The addition of quaternary onium salts in this photoreduction system enhances the H_2 evolution, where the onium salts with longer alkyl groups become more effective. Catalytic turnover number of TP for H_2 evolution after 3-h irradiation was significantly increased from 4.5 in the absence of salts to 31 in the presence of 80 mM of tetra-*n*-butyl-ammonium bromide. Dynamics studies of TP photosensitization reveal that the presence of the salts contributes to stabilization of the radical anion of TP ($TP^{\bullet-}$) formed through reductive quenching of the excited singlet state of TP ($^1TP^*$) and the triplet state of TP ($^3TP^*$) by TEA. The TP photosensitization accompanies competitive photo-Birch reduction (dearomatization of TP) via reaction between $TP^{\bullet-}$ and protone, but the presence of onium salts enhances the lifetime of $TP^{\bullet-}$ through the specific interaction, leading to the effective TP-photosensitized H_2 evolution. The presence of the soft onium cations with long alkyl groups stabilized the soft anion, $TP^{\bullet-}$, through electrostatic soft-soft intermolecular interaction.

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Potocorrosion at Single Crystal n-TiO_2 Rutile Electrodes: Mechanisms and Kinetics with relation to Crystal Structure

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Photoetching of n-TiO_2 rutile electrodes in competition with water photooxidation is only known to take place in aqueous sulfuric acid [1-2] and in Cr(VI) containing aqueous electrolytes at pH≤1 [3]. In both cases, the presence of a huge concentration of protons seems to be a necessary condition for efficient photocorrosion. Interestingly, a recent study with rutile wafers (001)-, (100)- and (110)-oriented shows that photoetching proceeds preferentially in the crystallographic <001> direction [2], along rutile structural channels where protons can easily move.

Photoetching involves Ti-O bonds breaking, which is only possible under accumulation of photogenerated holes at surface $O^{=}_{L,s}$ lattice ions [3]. This is not possible at neutral and basic pH because of the rapid inelastic hole transfer from O:2p valence band orbitals to chemisorbed water species ($O^{\bullet -}_{L,s} + H_2O \longrightarrow O^{=}_{L,s} + OH^{\bullet}_{s} + H^{+}_{aq}$). However, in contact with very acidic electrolytes, surface dangling bonds of $O_{L,s}$ species become saturated with protons, which gives rise to surface $OH_{a,s}$ hydroxyls acidic in character ($O^{=}_{L,s} + H^{+}_{aq} \longrightarrow OH^{-}_{as}$).

The anisotropic rutile photoetching in the <001> direction is discussed in terms of a multistep process leading to oxygen evolution from the lattice (Ti-O bonds breaking). This process is assumed to start with hole trapping by acidic $OH^{-}_{a,s}$ hydroxyls at structural channels, to generate $OH^{\bullet}_{a,s}$ radicals ($OH^{-}_{a,s} + h^{+} \longrightarrow OH^{\bullet}_{a,s}$). Further, surface bound peroxo species are generated from chemically interacting $OH^{\bullet}_{a,s}$ radicals ($OH^{\bullet}_{a,s} + OH^{\bullet}_{a,s} \longrightarrow (H_2O_2)_s$). Finally, peroxo species become photooxidized and oxygen from the lattice is evolved ($(H_2O_2)_s + 2h^{+} \longrightarrow 2H^{+}_{aq} + O_2\uparrow$). The rate limiting step of the global reaction ($2TiO_2 + 4h^{+} \longrightarrow 2(TiO^{2+})_{aq} + O_2\uparrow$) is covalent bonding between $OH^{\bullet}_{a,s}$ radicals. This step becomes catalyzed at the walls of structural channels, in the <001> direction, where the $O^{=}_{L}$-$O^{=}_{L}$ distance is the shortest one in the rutile structure (2.52 Å), which is far below the 3 Å critical $OH^{\bullet}$-$OH^{\bullet}$ distance for efficient H_2O_2 formation [5].

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INTERFACIAL STRUCTURE OF POLYCRYSTALLINE CdS FILMS IN AQUEOUS ELECTROLYTES.

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One advantage of photoelectrochemical cells is that the contact with a liquid phase makes no topographical restrictions and polycrystalline semiconductor materials can be employed as photoelectrodes. However, the surface of polycrystalline solids exposes grain boundaries that acts as recombination sites and/or as barriers to carrier transport, and the construction of efficient photoelectrochemical conversion devices requires a description of the polycrystalline semiconductor / electrolyte interface.

Here we present a detailed study of the interfacial (i.e. flat band potential, U_{fb}, and interfacial potential distribution) and electronic properties (i.e. carrier density, n_0, mobility, m, and intergrain barriers heights, E_B) of polycrystalline CdS films in contact with aqueous electrolytes. 300 nm thick films, prepared by controlled precipitation on a conductive substrate (ITO), are composed by 20 nm nanocrystals. Experimental information was collected from impedance spectra and surface conductance – potential plots in a wide bias range. Results from these complementary techniques were interpreted by considering a microscopic model that takes into account the contribution of grain length and intergrain barriers. In this way, we have determined the values for the characteristic parameters presented in the Table below.

We achieve an explicit evaluation of: (i) the effect of intergrain barriers in the surface and bulk charge transport across the films; (ii) the influence of applied potential on the intergrain barriers in contact with the electrolyte; (iii) the effect of intergrain barriers on the distribution on surface potential. From comparison with the behavior of single crystals it is concluded that in the depletion region the main effect of low crystal size and intergrain barriers is the reduction of both crystallite effective volume and electron surface excess. On the other hand, in the accumulation region there is an expansion of the space charge layer due to the lowering of intergrain barriers at the surface.

Characteristic parameters for polycrystalline CdS in aqueous 0.1 M Na_2SO_4

U_{fb} /V_{SCE},	n_0 / m^{-3}	m / $m^2\ V^{-1}\ s^{-1}$	E_B / eV
-0.43 ~ -0.15	10^{24} ~ 4 10^{24}	10^{-5} ~ 10^{-3}	0.17 ~ 0.29

Photoelectrochemical Behavior of n-GaAs and n-$Al_xGa_{1-x}As$ in CH_3CN

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ABSTRACT

Current density vs potential, open-circuit voltage vs temperature and differential capacitance vs potential measurements have been used to show that n-GaAs and n-$Al_xGa_{1-x}As$ electrodes exhibit partial Fermi level pinning in contact with CH_3CN over a wide range of redox potentials. Despite a change of over 1.2 V in redox potential of the solution, the open-circuit voltage only changed by ~300 mV. The slope of open-circuit voltage vs redox potential of the solution was typically 0.33-0.44. Differential capacitance vs potential data also yielded a barrier height change of less than 300 mV for over 1.2 V change in the redox potential of the solution. The dependence of the current density vs potential behavior of n-GaAs/CH_3CN-ferriceneium-ferrocene$^{+/0}$ on variables such as the illumination intensity, the dopant density of the semiconductor, the concentration of redox acceptor in the solution, the crystal face, the electrolyte, and the cell temperature was evaluated. The resultant kinetic data indicate that surface-state recombination is the dominant recombination mechanism at these interfaces that are capable of producing open-circuit voltage of 0.83 V at short-circuit current density of 20 mA cm^{-2}, and energy conversion efficiencies of > 10%. X-ray photoelectron spectroscopy investigation of n-GaAs confirmed surface changes induced by operation of n-GaAs electrodes in CH_3CN-cobaltocenium-cobaltocene$^{+/0}$ electrolyte. The presence of Fermi level pinning and existence of changes in n-GaAs and n-$Al_xGa_{1-x}As$ electrode surface when contacted with CH_3CN-cobaltocenium-cobaltocene$^{+/0}$ electrolyte complicate the extraction of k_{et} values from the steady-state current density vs potential behavior of n-GaAs or n-$Al_xGa_{1-x}As/CH_3CN$ contacts.

ELECTRON TRANSFER REACTIONS IN HYDROGEN GENERATION PHOTOSYSTEMS FOR THE CLEAVAGE OF WATER

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H_2 evolution by photochemical transformation and assemblies which effect water photodecomposition are described.

The photocatalytic cleavage of water, supramolecular photochemical assemblies, photosensitized electron-transfer reaction in colloidal microenvironments,photoinduced electron transfer reactions, the rate of electron hole pair generation by light absorption in spherical TiO_2 particles, comparison of the rate of electron generation with the maximal transport rate of oxygen by diffusion, limiting efficiencies of solar photolysis of water, photoelectrochemical H_2 evolution systems through water photolysis and thermal decomposition processes for hydrogen generation are presented .

Substantial progress has been made in the application of semiconductors as light active materials in photosensitized electron-transfer reactions, initiated by ionization under UV light.

TiO_2 has been shown to be most suitable material, offering the highest light-conversion efficiency. The special separation of an electron and a hole is promoted by the internal electric field in the semiconductor near-surface layer where the light is absorbed.

Theoretical considerations and practical aspects on water photolysis are discussed.

PREPARATION AND CHARACTERIZATION OF COPPER INDIUM DISELENIDE FILMS BY ELECTRO/ELECTROLESS DEPOSITION

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Polycrystalline solar cells based on Copper Indium Diselenide (CIS) film precursors have shown encouraging results in the recent past. Electrochemical deposition is a very useful technique for developing large area, low cost precursors. Therefore, preparation of CIS films by electrodeposition (ED) and electroless deposition (EL) assumes significant interest for developing economical solar cells. The preparation of CIS films by electroless deposition and electrodeposition techniques is reported. The films have been deposited on molybdenum coated glass substrates. The deposition bath consisted of aqueous solutions of copper chloride, indium chloride, selenous acid. The substrate was short-circuited with the Fe counter electrode for the electroless deposition while a potentiostat was used for electrodeposition. The films have been characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX), Inductively Coupled Plasma Spectroscopy (ICP), Auger Electron Spectroscopy (AES) and Optical spectroscopy. The results indicate that reasonable quality CIS films can be grown by a simple electroless deposition process followed by recrystallization in selenium atmosphere while very good quality CIS films can be grown by electrodeposition. These films were also characterized by electrochemical, photoelectrochemical and opto-electronic techniques. Photovoltaic structures were formed with ED as well as EL films after processing and recrystallization to adjust the film stoichiometry.

Key words: $CuInSe_2$, Electroless deposition, Electrodeposition, Thin Films, Polycrystalline solar cells.

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DEVELOPMENT OF CdTe BASED PHOTOVOLTAIC DEVICES ON LIGHTWEIGHT METALLIC SUBSTRATES AS AN ALTERNATIVE TO THE GLASS BASED STRUCTURES

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CdTe is a promising photovoltaic material due to its nearly optimum band gap and high absorption coefficient. There are various reports on growth and characterization of CdTe films on flexible substrates such as molybdenum (Mo) and stainless steel (SS). In the present study attempts were made to electrodeposit CdTe on SS and Mo substrates and evaluate the film properties. Effect of various deposition conditions on film properties and structure has been investigated. Schottky barriers (SS/CdTe/Au, Mo/CdTe/Au) as well as heterojunctions of SS/CdTe/CdS and Mo/CdTe/CdS were formed and studied. Completed cells have not yet been tested but the work on the heterojunction CdTe/CdS is in progress.

Good quality stoichiometric CdTe thin films of various thickness were deposited using the potentiostatic deposition technique. Prior to the deposition of CdTe; a thin inter layer of tellurium rich CdTe was electrodeposited on the metallic substrates which is expected to improve the contact between the type converted CdTe and the metal. In all the deposited films the transferred number of electrons for the deposition of one molecule of CdTe was found to be six, in good agreement with the theory. Compositional analysis was performed using an ICP system and the atomic percentage of Cd and Te for the as deposited films were approximately 50.5% and 49.5% respectively, showing that the film is nearly stoichiometric. I-V, C-V, XRD, SEM, AES, optical and opto-electronic analyses characterized the films and device structures. Auger depth profiles of the film revealed that when the nucleation of CdTe starts on the substrate the composition of Cd and Te is exactly 1:1 and afterwards the film is slightly rich in Cd except at the film surface. The surface of the film is rich in tellurium due to the formation of a Te rich oxide layer as is evident from the increase in oxygen content. The concentration of Te is constant throughout the thickness of the film.

The deep and shallow levels in the band gap were detected with the two novel techniques, photoinduced current transient spectroscopy (PICTS) and thermally stimulated current spectroscopy (TSCS). The PICTS is a powerful technique to study the deep levels in high resistivity materials. The electron and hole traps were distinguished by illuminating the device with a highly absorbing radiation, then depending on the applied polarity the electrons or holes will be injected in to the bulk of the material and get trapped. By observing the peaks in the PICTS spectrum with respect to the applied polarity, the type of the detected traps were identified.

Improving the Photoelectrochemical Performance of Nanostructured TiO_2 Films.

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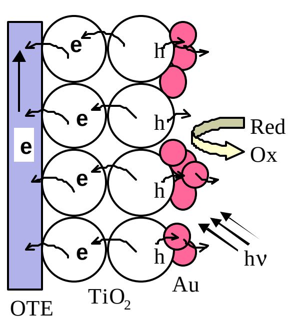
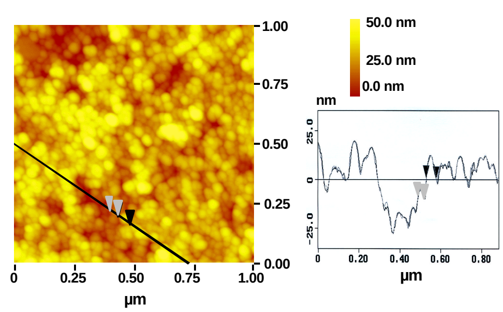
Photoinduced deposition of noble metals such as Pt or Au on semiconductor nanoclusters has often been employed to enhance their photocatalytic activity. For example, deposition of a noble metal on semiconductor nanoparticles is an essential factor for maximizing the efficiency of photocatalytic water splitting reactions. The noble metal (e.g., Pt), which acts as a sink for photoinduced charge carriers, promotes interfacial charge transfer processes. We have now investigated the effect of metal deposits on the photoelectrochemical properties of nanostructured semiconductor films. Such semiconductor-metal composite films can play an important role in improving the performance of photoelectrochemical cells

Thin films of TiO_2 were cast on conducting glass plates (OTE) by applying a colloidal suspension followed by annealing at 673K. Gold nanoparticles (5 nm diameter) were prepared in toluene using a phase transfer catalyst, tetraoctylammonium bromide. The electrodes were immersed in gold nanoparticle suspension for 4-6 hours as the gold nanoparticles got deposited on the TiO_2 particulate film. The pink coloration of the film along with the presence of a surface plasmon absorption band at 546 nm confirmed the presence of gold nanoparticles on the TiO_2 films. Both AFM and SEM studies indicate the presence of islands of gold nanoclusters on the TiO_2 surface. The maximum IPCE observed for OTE/TiO_2/Au electrode at 320 nm is around 50% which is 3 times greater than the OTE/TiO_2 electrode.

The present study shows that semiconductor-metal composite films are capable of achieving improvements in the photoinduced charge separation and in the overall photoconversion efficiency. The adsorbed gold nanoparticles play an important role in maximizing the photocurrent generation by facilitating hole transfer to the redox couple and increasing the photovoltage by ~150 mV by shifting the apparent Fermi level to more negative potentials. The observed 3-fold enhancement in the photoconversion efficiency has important applications in dye-sensitized solar cells and photocatalytic reactions.





Left: Charge Separation in a old nanoparticle modified Nanostructured TiO_2 Electrode.

Right: Atomic Force Microscopy of TiO_2 nanostructured film modified with gold nanoparticles. The cross section view shows the presence of larger gold particles (50-70 nm) at the surface.

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ELECTROCHEMICAL SYSTEM ON BASIS OF NANOSTRUCTURED INDIUM PHOSPHIDE FOR CONVERSION OF SOLAR ENERGY

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The photoelectrochemical properties of nanostructured semiconductor InP electrode in polysulfide solutions are investigated. The nanostructured surface InP was created by selective chemical etching. After a chemical etching of InP on its surface was deposited the layer of nanosized CdS particles by a method of a chemical deposition. The thickness of this layer varied from 2 up to 10 nm. Is found, that at optimal width of a CdS layers 3 - 4 nm, the open circuit voltage in the electrochemical cell containing the polysulfide solution is increased on 0,20 - 0,30 V on a comparison with an InP electrode which is not containing surface layer CdS. At the same time the velocity of a surface recombination decreases on 1-2 order. After a deposition of CdS layer the efficiency of a solar energy conversion on InP-electrode has increased from 14 % up to 20 %.

Is shown, that the composition of polysulfide electrolyte essentially influences an overall performance of the solar cell. For description of a chemical equilibrium in an electrolyte the processes of ionic pairing between ions S^{2-} (HS^-) and cations K^+ and Na^+ were taken into account.. The distribution of ions in polysulfide solutions of various concentrations is defined. The composition of an electrolyte permitting to increase efficiency of solar energy conversion and stability of nanostructured InP electrode is developed.